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Verhoeven, VWA; Van Vondel, MPY; Ganzeveld, KJ; Janssen, LPBM

Published in:
Polymer Engineering and Science

DOI:
[10.1002/pen.20163](https://doi.org/10.1002/pen.20163)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2004

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Verhoeven, VWA., Van Vondel, MPY., Ganzeveld, KJ., & Janssen, LPBM. (2004). Rheo-kinetic measurement of thermoplastic polyurethane polymerization in a measurement kneader. *Polymer Engineering and Science*, 44(9), 1648-1655. <https://doi.org/10.1002/pen.20163>

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Rheo-Kinetic Measurement of Thermoplastic Polyurethane Polymerization in a Measurement Kneader

V. W. A. VERHOEVEN, M. P. Y. VAN VONDEL, K. J. GANZEVELD,
and L. P. B. M. JANSSEN*

*Department of Chemical Engineering
University of Groningen
Nijenborgh 4, 9747 AG, Groningen, The Netherlands*

The rheo-kinetics of thermoplastic polyurethane (TPU) formation was investigated in a measurement kneader at high temperatures. The TPU was made of a polyester polyol, methyl-propane-diol and a 50/50 mixture of 2,4'- and 4,4'-diphenylmethane diisocyanate (MDI). The reaction proceeded according to a second order reaction for which the kinetic constants were determined by size exclusion chromatography (SEC) analysis. The activation energy was found to be equal to 61.3 kJ/mol, and the pre-exponential factor was equal to 2.18×10^6 mol/kg K. For the temperature range under investigation, the flow activation energy was equal to 42.7 kJ/mol, which is comparable to that of a linear polymer. This indicates that the hard segments are completely dissolved at the temperatures investigated. The initial part of the reaction was much faster than anticipated from the kinetic measurements. Diffusion limitations at higher conversions probably cause this decrease in reaction velocity. At longer reaction times, the molecular weight leveled off because of depolymerization. Therefore, additional experiments are necessary to describe the complete polymerization of thermoplastic polyurethane. *Polym. Eng. Sci.* 44:1648–1655, 2004.

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INTRODUCTION

Thermoplastic polyurethane (TPU) is a versatile elastomer that is used in automotive products, electronics, glazing, footwear and for industrial machinery. A common production method for thermoplastic polyurethane is reactive extrusion. Monomers are fed to the extruder by a precise metering system. In the extruder, reaction and transport take place, and the polymer formed is pelletized at the die. These TPU-extruders are, to the best of our knowledge, mainly operated on the basis of experience. This empirical approach is caused by the fact that flow and reaction are directly connected in an extruder, which makes the prediction of the outcome of a reactive extrusion process a difficult task. Moreover, the fact that numerous combinations of monomers and catalysts are used to produce a variety of TPUs does not make the situation more ordered.

Therefore, to control the extruder process, a reliable extruder model in combination with reliable kinetic knowledge of the system used would be a considerable improvement.

However, to establish reliable kinetics of thermoplastic polyurethane polymerization is not a straightforward task. The monomers from which thermoplastic polyurethane is produced are poorly miscible. Therefore, a combination of diffusion and reaction determines the reaction rate observed for every kinetic measurement. Diffusion limitations will be most noticeable during the initial part of the reaction and at high conversions. In the early phase of the reaction, mixing will enhance the observed reaction velocity, through improvement of the micro-stoichiometry and through enlargement of the contact surface of the immiscible monomers. At the end of the reaction, the mobility of the end-groups and of the catalyst is much lower because of the large polymer molecules that have formed. This limited diffusion at high conversions may also have an impact on the reaction velocity observed. Moreover, as a consequence of the competition between diffusion and reaction, the kinetic measurements for TPU polymerization are best performed at the temperature and the mixing situation

*To whom correspondence should be addressed.

E-mail: L.P.B.M.Janssen@chem.rug.nl

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Published online in Wiley InterScience (www.interscience.wiley.com).

DOI: 10.1002/pen.20163

of the application for which the kinetic investigation is intended. For instance, for reactive injection molding the reaction takes place at temperatures between 30°C and 120°C, the reaction mass experiences initially a high shear, and after the injection the reaction mass remains stagnant. Adiabatic temperature rise experiments (ATR), which are performed under the same conditions, are, therefore, best suited to establish the kinetics in this situation.

Applying this analogy to reactive extrusion, it would mean that kinetic measurements should be performed under shear conditions and at high temperatures (150°C–225°C). These conditions are met in a rheometer and in a measurement kneader. However, neither instrument is specifically designed for kinetic measurements. Measurement kneaders, for instance, are mostly used for (reactive) blending of polymers, as was done by Cassagnau *et al.* (1) or for rubber research (2). Both the rheometer and the measurement kneader have a drawback if they are used for kinetic measurements: the extent of reaction in both instruments can be followed only indirectly through the increase in torque. In order to correlate the torque to conversion, a calibration procedure is necessary, for which samples must be taken. An additional simultaneous measurement of conversion in the rheometer or kneader would make this sampling procedure superfluous. Unfortunately, no obvious method is available. An adiabatic method as applied by Lee *et al.* (3) or Blake *et al.* (4) is not apt, owing to the lack of heat production at higher conversions. A combination of rheology with a spectroscopic method, for example with fiber-optic IR or Raman spectroscopy, has not been reported yet for polyurethanes. However, the accuracy of such a method might not be sufficient at high conversion, and a stagnant polymer layer may form on the measurement cell.

In the comparison between a rheometer and a kneader, a rheometer seems better fit for rheo-kinetic measurements, since, in a rheometer, the viscosity can be measured directly. Nevertheless, a measurement kneader is preferred in this research because:

- The mixing behavior in a kneader resembles the mixing behavior in an extruder more closely, with both dispersive and distributive mixing action.
- Sampling of a small amount of material does not disturb the measurements in a kneader, whereas rheology measurements are gravely affected by sampling.
- Sampling of viscous material may damage the cone and plate in a rheometer.
- Temperature control in a kneader is straight-forward. In a rheometer, temperature control becomes complicated at temperatures above 150°C since both cone and plate must be heated in that case.
- Highly viscous material can be processed easily in a kneader, while in a rheometer, constant shear

experiments at shear rates that are comparable to those in an extruder are sensitive to edge failure and demand a high torque range.

In several studies the kinetics of TPU polymerization is measured under mixing conditions (3–8). All of these measurements were performed at relative low temperatures (< 90°C) and mostly on crosslinking systems. Therefore, no high conversions could be reached, since the glass temperature or the gelation temperature was reached reasonably early in the reaction (around 70% conversion). Kinetic methods that do reach high conversions are largely “zero-shear” methods. As for radical polymerization (9) little attention has been paid to the interaction between mixing and reaction. Often it is expected for step polymerization that shear does not have an impact on the reaction velocity, owing to the relative high mobility of the reactive end groups in a polymer chain. Malkin *et al.* (10), for instance, state that any observed acceleration of reaction speed for polycondensation reactions can almost always be ascribed to viscous heating of the reaction mass.

Schollenberger *et al.* (11) performed the only study known in a measurement kneader. Unfortunately no quantitative data were obtained in this study. So no reliable kinetic data exist on TPU polymerization in an extruder, even though this is a large industrial process. Therefore, this article focuses on the acquisition of relevant kinetic data for extruder modeling. A new method is presented, which is based on experiments in a measurement kneader. In a kneader, measurement conditions are more similar to those in an extruder in comparison to existing kinetic measurement methods. Quantitative kinetic and rheological data can be obtained through this method; moreover, the effect of mixing on the polymerization reaction can be investigated.

EXPERIMENTAL

Kneader

The kneader used in this research was a Brabender W30-E measurement mixer. The mixer consists of two triangular paddles that counter-rotate in a heated barrel. The barrel can be closed with a (heavy) plug. The volume of the kneader is 30 cm³. The kneader is driven by a Brabender 650-E Plasticorder. Two heating elements in combination with two control thermocouples (one in the back-plate and one in the kneader section) keep the kneader on the set temperature (T_{set}). A thermocouple sticking in the non-intermeshing zone of the kneading chamber is used for the measurement of the melt-temperature ($T_{measure}$). Torque and temperature development in the kneader can be followed by means of a data-acquisition system.

Experimental Method

Preparations Before an Experiment

The TPU system for the experimental analysis reviewed in this paper consisted of:

- A polyester polyol of mono-ethylene glycol, di-ethylene glycol and adipic acid ($M_w = 2200$ g/mol, $f = 2$)
- Methyl-propane-diol
- A 50/50 mixture of 2,4-MDI and 4,4-MDI ($f = 2$).

The percentage of hard segments was 24%. The reaction was catalyzed using bismuth octoate. Both the polyester polyol as the methyl-propane-diol were dried at 60°C with molecular sieves (0.4 nm) prior to use. The isocyanate was used at 50°C.

Just before an experiment the polyol, diol, isocyanate and catalyst were weighed in a paper cup and mixed, using a turbine stirrer at 2000 rpm for 15 seconds. Experience showed that this premixing was necessary to obtain reproducible results. About 30 grams of the premixed reaction mixture was transferred to the kneader with a syringe. The exact amount of reaction mixture was determined by weighing the filled syringe before and after emptying. The kneader measurement was started upon filling.

Sampling

In order to relate torque to molecular weight, samples were taken and analyzed (see Theory of Kinetic Measurement). The sampling method consisted of removing the stamp of the kneader, collecting the sample with tweezers, followed by quenching the material in liquid nitrogen. After taking a sample the stamp was put back on the kneader; the whole sampling routine had a negligible influence on the torque during a very short period. In order to inactivate the still reactive isocyanate end-groups, the samples were dissolved in THF with 5% di-butylamine. The samples were subsequently dried and used for size exclusion chromatography analysis.

Size Exclusion Chromatography (SEC)

Samples were analyzed for their molecular weight distribution by size exclusion chromatography (Polystyrene calibrated). The chromatography system consisted of two 10 μ m Mixed-B columns (Polymer Laboratories) coupled to a refractive index meter (GBC RC 1240). The columns were kept at 30°C. Tetrahydrofuran (THF) was used as eluent and its flow rate was set to 1 ml/min. The molecular weight distribution was analyzed using Polymer Laboratories SEC-software version 5.1. About 25 mg of polymer was dissolved in 10 ml of THF; the dissolved samples were filtered on 0.45- μ m nylon filters.

THEORY OF KINETIC MEASUREMENT

The objective of this study is to determine the reaction rate constant under mixing conditions for the thermoplastic polyurethane under investigation. Therefore the torque and temperature curves measured in the kneader must be translated into a time-dependent conversion curve. For condensation polymerization conversion, molecular weight and viscosity are related in a

straightforward way. However, it is impossible to derive the conversion directly from the viscosity. This is called the "direct rheo-kinetic problem" by Malkin (4). The relationship between viscosity and molecular weight has to be established first, before conclusions can be drawn on the reaction pattern. In addition, there is a complicating factor in a measurement kneader. Owing to the complicated flow profile in a kneader, it is not immediately clear how the measured torque can be related to the viscosity. Nevertheless, a (simplified) flow analysis can tackle this problem. Subsequently, the relationship between the torque and the molecular weight can be established.

Rheology Basis

A simplified model of the kneader forms the basis of the flow analysis. The true geometry of the kneader is simplified as in Fig. 1. The shear stress can then be calculated using a flat-plate approach for which the paddle is considered to be stationary and the barrel moves with a velocity V_b . The shear stress at the wall is then equal to:

$$\tau = -\eta_{app} \dot{\gamma} = -\eta_{app} \left(M \frac{N\pi D}{H} \right) \quad (1)$$

The factor M can be calculated through a flow analysis, for which the height H is a function of the angular coordinate. The viscosity is written as the apparent viscosity, since for our polymeric material a Newtonian approach is inaccurate. The value of the torque acting on a paddle is opposite to the torque value experienced by the barrel wall and is equal to the force acting on the wall times the lever arm.

$$\begin{aligned} \text{Torque} &= (\text{Area} \cdot \text{Shear Stress}) \cdot \text{Lever Arm} \\ &= (\pi DW \cdot \tau) \cdot (D/2) \end{aligned} \quad (2)$$

For two paddles this equals:

$$\text{Torque} = \frac{M\pi^2 D^3 W}{H} \cdot N \cdot \eta_{app} = C \cdot N \cdot \eta_{app} \quad (3)$$

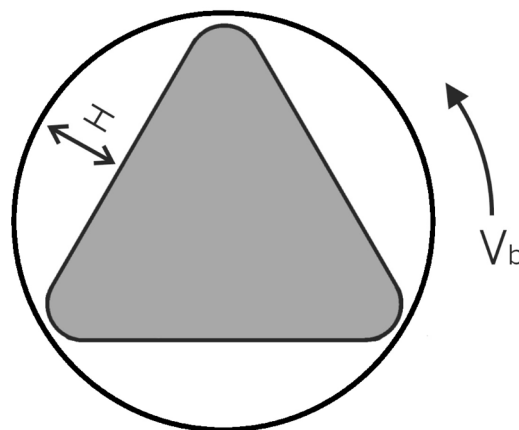


Fig. 1. Simplification of the flow situation in the measurement kneader.

C can be considered as a geometry factor. The manufacturer of the kneader gives a similar equation to correlate torque to viscosity, with the constant C equal to 50. Equation 3 shows that for a Newtonian fluid, the torque is directly proportional to the apparent viscosity of the material in the kneader. If we consider the polyurethane as a power-law liquid, Eq 3 can be rewritten as:

$$\text{Torque} = C' \cdot N^n \cdot \eta_0 \quad (3a)$$

The next step that is necessary for tackling the direct rheo-kinetic problem is to correlate the viscosity of the polymer to its weight average molecular weight. It is well established experimentally as well as theoretically that for an "entangled" linear polymer:

$$\eta_0 = A(T) \cdot M_w^{3.4} \quad (4)$$

$A(T)$ is a proportionality-factor that is temperature dependent. For linear amorphous polymers $A(T)$ can be described with a Williams-Landel-Ferry-equation (WLF-equation) or with an Arrhenius-type of expression. In general for a temperature less than 100°C above the glass transition temperature (T_g) of the polymer, a WLF-equation is preferable; for higher temperatures an Arrhenius-type expression is best-suited (12). For polyurethanes the value of T_g is dependent on the specific chemicals used, but for most polyurethanes T_g does not exceed 320 K (13). An Arrhenius-type of expression should therefore be apt to describe the temperature dependence of viscosity for the temperature range under consideration (400–475 K).

If Eqs 3a and 4 are combined, the following equation appears:

$$M_w = \left(\frac{\text{Torque}}{A'(T)} \right)^{\frac{1}{3.4}} \quad \text{with} \quad A'(T) = A(T) \cdot C' \cdot N^n \quad (5)$$

The torque is now related to the molecular weight. If the function $A'(T)$ is known, the weight average molecular weight versus time for the TPU-reaction can be calculated from the logged torque and temperature values. In analogy with the temperature dependence of the viscosity, the temperature dependence of $A'(T)$ can be described with an Arrhenius-type equation:

$$A'(T) = A_0 \cdot e^{\frac{U_A}{R \cdot T}} \quad (6)$$

In order to relate torque to molecular weight, the flow activation energy (U_A) and pre-exponential factor (A_0) in Eq 6 must be known. These constants can be found through a "calibration procedure." For this procedure, samples are taken from the kneader and analyzed for their molecular weight with size exclusion chromatography (SEC). Samples of different molecular weights and samples taken at different reaction temperatures are necessary for the procedure. The molecular weight can be calculated from torque and temperature (T_{measure}) values using Eqs 5 and 6. The calculated and measured molecular weight can be compared, and the optimal value for A_0 and U_A can be found through a least-square fitting routine.

Kinetic Basis

From the molecular weight versus time curve, the kinetics of TPU-polymerization can be obtained. Although the exact reaction mechanism is more complex, the TPU polymerization reaction is often described successfully with a second order rate equation (14). For a second order polymerization reaction (assuming equal amounts of alcohol and isocyanate groups, equal reactivity of P765 and the chain extender and a Flory molecular weight distribution) the weight average molecular weight increases in time according to:

$$M_w = M_{\text{rep}} \cdot (1 + 2 \cdot [\text{NCO}]_0 \cdot k(T, [\text{cat}]) \cdot t) \quad (7)$$

In this equation M_{rep} is the molecular weight of a repeating unit (equal to 628) and $[\text{NCO}]_0$ is the initial isocyanate concentration. Equation 7 shows that the molecular weight increases linearly in time. Since M_{rep} and $[\text{NCO}]_0$ are constants, the slope of the molecular weight versus time curve is proportional to the (apparent) reaction rate constant $k(T, [\text{cat}])$:

$$\frac{dM_w}{dt} = 2 \cdot M_{\text{rep}} \cdot [\text{NCO}]_0 \cdot k(T, [\text{cat}]) \quad (8)$$

In case A_0 and U_A are known, the torque versus time graph can be translated in a molecular weight versus time graph (Eq 5). From the slope of this curve and through applying Eq 8, the value of the reaction rate constant can be calculated. If experiments are performed at different temperatures and at a constant catalyst level, an Arrhenius-expression can be established for the reaction rate constant.

There is just one limitation. According to Eq 7, the molecular weight will rise to infinity at longer reaction times. In practice this will not happen. Several phenomena may cause a leveling off of the molecular weight and torque values at longer reaction times:

- The initial ratio of alcohol groups to isocyanate groups will never be exactly unity. This stoichiometric imbalance will limit the maximum conversion.
- Chain scission. The long molecules that are present at longer reaction times are prone to scission as a result of shearing.
- Depolymerization. It is generally accepted that the rate of depolymerization is dependent on urethane concentration through a first order rate equation. As the concentration of urethane bonds is high at longer reaction times, the rate of depolymerization will gain importance. For every temperature there is an equilibrium molecular weight at which the forward reaction is equally fast as the reverse reaction. At that temperature the molecular weight will not rise to a higher value. Depolymerization is reported to have an effect starting at 150°C (15, 16).
- Allophanate formation. The high concentration of urethane bonds together with the continuous presence of a small portion of free isocyanate groups

due to depolymerization can give rise to allophanate formation. Allophanate formation causes branched molecules. Polydispersity will therefore increase, but since the stoichiometry of reactants is also affected, the net effect on the molecular weight is not clear. Because of branching, the A-factor in Eq 4 may change.

- A last reason why M_w will not rise to an infinite value is degradation. This will of course limit the maximum M_w .

All of the factors mentioned above gain importance at longer reaction times and at higher molecular weights. Therefore reliable kinetic data in the measurement kneader is best obtained during the initial stage of the reaction.

RESULTS

A Typical Kneader Experiment

Figure 2 shows a typical graph obtained for a kneader experiment. The torque and the temperature are shown as a function of time. As expected, the torque increases in time because of the polymerization reaction. The torque curve in Fig. 2 reaches a steady value after 15 minutes. After an initial drop due to filling of the kneader, the temperature also rises steadily to a constant value. Clearly, viscous dissipation plays an important role in the kneader; the dissipated heat cannot be completely removed through the walls. In general, the measured temperature exceeds the set temperature (in Fig. 1, $T_{set} = 175^\circ\text{C}$). Analysis of the experimental curves shows that the temperature increase due to viscous dissipation ($\Delta T_{viscous} = T_{measure} - T_{set}$) is proportional to the torque value with a proportionality factor of $2^\circ\text{C}/\text{Nm}$.

The Determination of the Flow Activation Energy and the Pre-exponential

The torque-temperature graph can be converted into a molecular weight versus time graph using Eq 5. To do

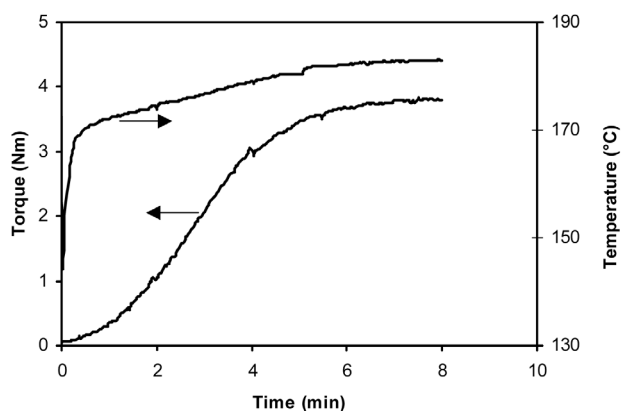


Fig. 2. The torque and temperature versus the time in the measurement kneader. $T_{set} = 175^\circ\text{C}$, 80 rpm.

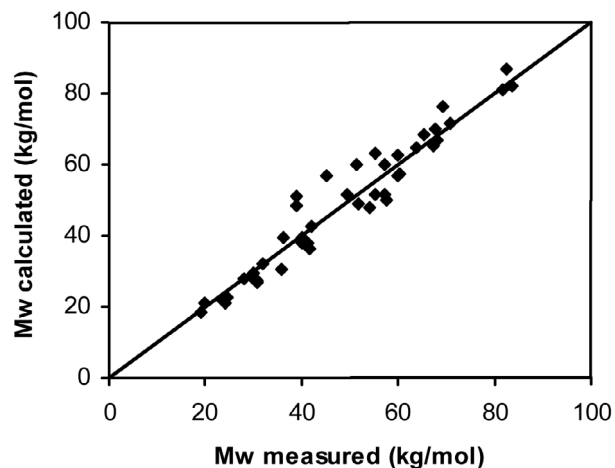


Fig. 3. Parity plot for the calculated and measured molecular weight.

so the function $A'(T)$ must be known, which means that the flow activation energy (U_A) and flow pre-exponential factor (A_0) must be established. To determine these constants, experiments were performed at four different set temperatures (125°C , 150°C , 175°C , 200°C). Every experiment was repeated three times; 4 to 5 samples were taken per experiment at different reaction times. The molecular weights of these samples have been determined, and obviously the value of the torque and the temperature at the moment a sample was taken is also known. U_A and A_0 can now be established by fitting the measured molecular weight to Eqs 5 and 6, with U_A and E_A as the fit parameters. Figure 3 shows the resulting parity plot in which the measured molecular weight is plotted against the calculated one. For the whole range of molecular weights the agreement is good.

The values obtained for U_A and A_0 are respectively 42.7 kJ/mol and $7.2\text{e-}22 \text{ N}\cdot\text{m}\cdot\text{mol}^{3.4}/\text{g}^{3.4}$ (see also Table 1). In general, thermoplastic polyurethanes have a much higher flow activation energy than expected for linear polymers. The hard segments that are present in thermoplastic polyurethanes provoke this effect. Hard segments are associated in hard domains and are physically crosslinked, which gives rise to a higher resistance to flow. Dissociation of the hard domains takes place at temperatures between 150°C and 200°C , depending on the composition of the polyurethane. Beyond that temperature the flow behavior will be that of a normal linear polymer. However, for the polymer under investigation the hard segments will probably dissociate at a much lower temperature. This is caused by the relatively low percentage of hard segments (24%) and the composition of the hard segments. The hard

Table 1. The Flow and Kinetic Parameters for the TPU Under Investigation.

U_A (kJ/mol)	42.7	E_A (kJ/mol)	61.3
A_0 ($\text{N}\cdot\text{m}\cdot\text{mol}^{3.4}/\text{g}^{3.4}$)	$7.2\text{e-}22$	k_0 (mol/kg K)	$2.18\text{e}6$

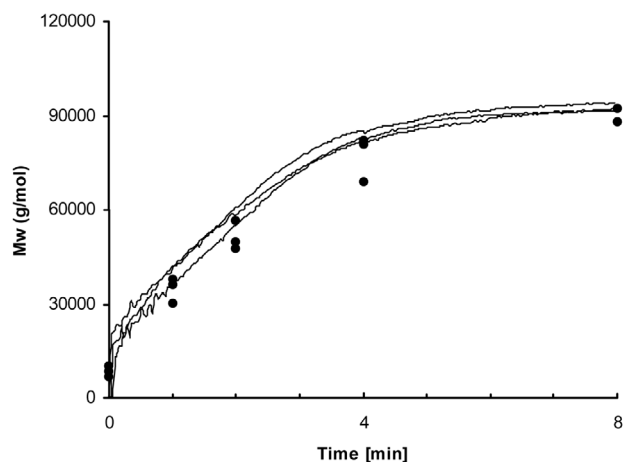


Fig. 4. The weight average molecular weight versus time in a measurement kneader. $T_{set} = 175^{\circ}\text{C}$, 80 rpm.

segments are built from a bulky chain extender and an isocyanate blend containing 50% 2,4-MDI. Steric hindrance, therefore, complicates association of the hard segments and improves the compatibility of the hard and soft segments. The flow activation energy found (42.7 kJ/mol) confirms this expectation, as it falls within the expected range for linear polymers (17). This result implies that for the TPU under investigation the hard segments are molten and completely dissolved in the soft segments, already at 125°C .

The Determination of the Reaction Rate Constant

The torque and temperature versus time curves of Fig. 2 can be translated into a plot of molecular weight versus time through applying Eqs 6 and 7. Figure 4 shows this plot for three replicate experiments at 175°C . The lines represent the molecular weights as calculated from the torque and temperature and the dots are the measured molecular weights. The agreement between the three experiments is reasonably well. In general the reproducibility was somewhat better at higher temperatures. Long reaction times in combination with higher molecular weights seemed to

deteriorate the reproducibility. The initial slopes are straight, which supports the second order assumption of the rate equation.

The reaction rate constant can be derived from the relation between molecular weight and time by determining the initial slope of the curves (e.g. in Fig. 4 the average slope between 0 and 4 minutes). As stated earlier, the initial slope gives the most reliable kinetic information. In Table 2 the different slopes with their confidence intervals are shown as well as the value for the reaction rate constant k . The reaction rate constant is calculated using Eq 8. It increases, as expected, with increasing temperature. The temperature in Table 2 is the measured temperature, $T_{measure}$. Since the kneader does not operate completely isothermally, there is always a temperature range over which the slope is determined. The mentioned temperature, $T_{measure}$, is the average temperature over which the slope is measured. This temperature range never exceeded 5°C .

Now, the kinetic constants can be derived from an Arrhenius plot (Fig. 5). The values obtained for E_A and k_0 are respectively 61.3 kJ/mol and 2.18×10^6 mol/kg K (see also Table 1). Three conclusions can be drawn from Fig. 5 and Table 1. First, the straight line in the

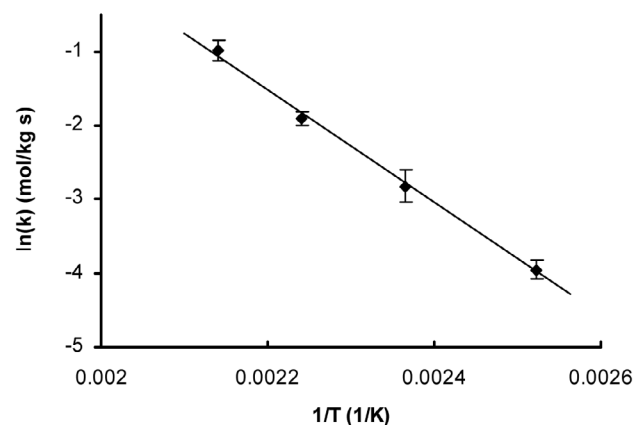


Fig. 5. The Arrhenius-plot for the kneader experiments.

Table 2. The Slopes and the Kinetic Results Obtained From the Kneader Experiments.

Temperature ($^{\circ}\text{C}$)	Slope (M_w/min)	Average Slope/1000 (M_w/min)	k (kg/mol s)
194.3	42,154 47,070 44,246	44 ± 6	0.37 ± 0.06
173.4	17,030 17,684 18,316	17.6 ± 1.6	0.147 ± 0.014
149.6	7134 6546 7784	7.2 ± 1.6	0.060 ± 0.012
123.3	2172 2416 2332	2.3 ± 0.4	0.0192 ± 0.002

Arrhenius-plot is an extra confirmation that the second order rate equation holds for the temperature range considered. Second, the value of E_A falls within the range reported for TPU-polymerization (30–100 kJ/mol). The scatter in activation energies reported in the literature is caused by the different catalysts and chemicals used. Finally, the plot shows that within the experimental uncertainties that are inevitable for measurement kneader experiments, quantitative kinetic and rheological results can be obtained.

Evaluation of the Kinetic Model

Model predictions are compared to experimental data in Fig. 6, in order to check the correctness of the kinetic parameters obtained. The slopes of the model prediction and of the experimental results are in good agreement with each other, which is a confirmation of the kinetic data.

However, as well at the start of the reaction as near the end of the reaction, model and experiment do not coincide. A detailed look at the starting point of the reaction reveals that the initial molecular weight is much higher than anticipated. For this reason, the model equation (Eq 7) is adapted in Fig. 6, to correct for the initial high molecular weight:

$$M_w = 17,000 + M_{rep} \cdot (1 + 2 \cdot [NCO]_0 \cdot k(T, [cat]) \cdot t)$$

The value of 17,000 for the molecular weight at $t=0$ is for all temperatures the same, and is fitted to the experimental curves. This correction is needed, since at the start of the measurement, the reaction has already started because of the premixing procedure. However, the molecular weight at the start of the measurement is unexpectedly high. A calculation reveals that, with the kinetic constants obtained in this research, the molecular weight after the premixing procedure should not exceed 1500.

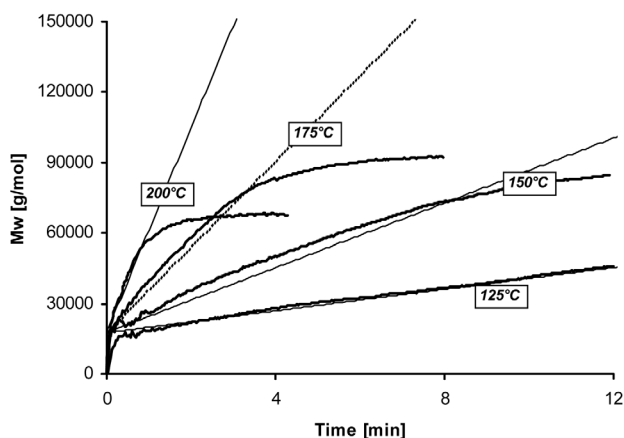


Fig. 6. The measured and calculated weight average molecular weight versus time.

The difference corresponds to an observation that other authors (15, 18) have also made for TPU-polymerization. The initial low-viscosity part of the reaction proceeds much faster than the last high-viscosity part of the reaction. This observation has been verified through ATR-experiments for this system (data not shown). With an initial temperature of 50°C and the same catalyst level as for the kneader experiments, the reaction reaches a conversion of about 80%–90% within 30 seconds. The explanation of the tremendous decrease in the observed reaction velocity at higher conversions falls under the term “diffusion limitation.” As soon as high molecular weight material appears, the mobility of the catalyst or the end groups decreases, which causes a decrease in the reaction velocity. The exact nature of this phenomenon cannot yet be understood, because of the limited range of these experiments. This problem will be the subject of further experimental research.

At the end of the reaction the experimental molecular weight levels off to a steady value. It is improbable that the initial stoichiometric deviation of at most 0.2% is the cause of this. An imbalance of 0.2% in stoichiometry leads to an equilibrium molecular weight of 350,000, which is much higher than the maximum molecular weight reported for this investigation. For the two high-temperature runs it is very probable that depolymerization has a major impact on the last part of the reaction and that, therefore, the reverse reaction is the predominant cause of the leveling of the M_w -curve. For the two low-temperature runs the situation is less distinct. Figure 4 shows that for the 200°C and 175°C experiments a higher temperature leads to a lower “equilibrium” molecular weight. This trend is hardly visible for the 150°C run and not visible at all for the 125°C run, because these runs are not completed within the time shown. Longer reaction times are here necessary to get to an equilibrium situation. Unfortunately, the results at long reaction times are less reproducible. The color of the polymer coming out of the kneader is light brown/yellow but deepens at longer reaction times. Degradation, therefore, interferes with experiments that last longer. An obvious indication of allophanate formation has not been found.

The kinetic model obtained in this research appears to have a limited validity. Still, if the reaction time is considered, an important part of the reaction is captured with this model. The initial, fast reaction takes only 5% of the total reaction time. Therefore, to predict the necessary residence time in an extruder, the kinetic model obtained in this study is indispensable. However, an expansion of the model is desirable. At low conversions, the reaction proceeds much faster than the measured kinetic data indicate. On the contrary, at very high conversions, the reaction stops, while the kinetic model predicts a continuous increase of the molecular weight. For the low conversion part, adiabatic temperature experiments must be performed to get the kinetic constants for this part of the reaction. Subsequently, these data can be combined with the data obtained from the

kneader in order to complete the kinetic model. For the very high conversion part of the reaction, the depolymerization reaction must be taken into account. Future experimental work will be directed towards depolymerization and low conversion experiments.

CONCLUSIONS

A kinetic investigation on TPU polymerization was performed in a measurement kneader. Quantitative kinetic and rheological data were obtained using this method. The method has advantages over other kinetic measurement methods since the reactants are mixed during an experiment, mimicking real processing circumstances. Therefore, for applications where the reaction takes place under mixing conditions, as for reactive extrusion, the kinetic parameters obtained will be more accurate. Besides, the effect of mixing on the polymerization reaction can be investigated with this method.

The kinetic data obtained proved that a second order reaction can be used to describe TPU polymerization. The experiments indicated that a fast initial reaction is followed by a slower "high conversion" part of the reaction. At the end of the reaction, the molecular weight levels off because of depolymerization and degradation. More experiments are necessary to take these effects into account.

Because of the complex geometrical form of the kneader, the viscosity-value obtained with a measurement kneader, is not very accurate. Therefore no attempt has been made to correlate the torque values to viscosity values. Nevertheless, the activation energy of flow could be established. The activation energy of flow falls within the range expected for linear polymers, which indicates that the hard segments are completely dissolved in the soft segments.

NOMENCLATURE

A_0	Flow pre-exponential constant ($\text{N}\cdot\text{m}\cdot(\text{mol/g})^{3.4}$)
$A(T)$	Empirical constant which relates viscosity to M_w ($\text{Pa}\cdot\text{s}\cdot(\text{mol/g})^{3.4}$)
$A'(T)$	Empirical constant which relates torque to M_w ($\text{N}\cdot\text{m}\cdot(\text{mol/g})^{3.4}$)
[cat]	Catalyst concentration (mg/g)
C, C'	Geometry factor of the kneader (m^3)
D	Diameter of barrel (m)
E_A	Reaction activation energy (J/mol)
H	Average difference of height between barrel and paddle (m)
k_0	Reaction pre-exponential constant (mol/kg s)

M_{rep}	Average weight of repeating unit (g/mol)
M_w	Weight average molecular weight (g/mol)
n	Power law index (-)
N	Rotation speed (1/s)
[NCO]	Concentration isocyanate groups (mol/kg)
$[\text{NCO}]_0$	Initial concentration isocyanate groups (mol/kg)
R	Gas constant (J/mol K)
T	Temperature (K)
T_g	Glass transition temperature (K)
$T_{measure}$	Measured temperature of the material in the kneader (K)
T_{set}	Set temperature of the kneader (K)
Torque	Torque (N·m)
t	time (s)
U_A	Flow activation energy (J/mol)
V_b	Barrel velocity (m/s)
W	Width barrel (m)
$\dot{\gamma}$	Shear rate (1/s)
η_{app}	Apparent viscosity ($\text{Pa}\cdot\text{s}$)
η_0	consistency ($\text{Pa}\cdot\text{s}^n$)
τ	Shear stress (Pa)

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